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The Variscan garnet peridotites from the Eastern Alps (Ulten Zone): records of subduction metasomatism in the mantle wedge

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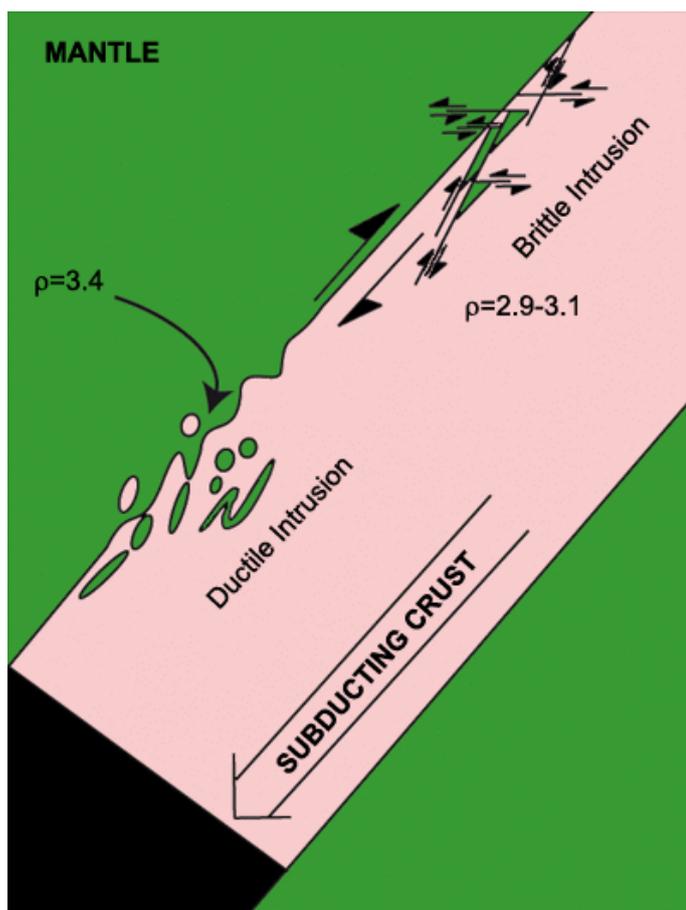
Abstract: At subduction zones, influx in the mantle wedge of fluids released by subducting plates affects the properties and composition of large mantle domains. These effects are investigated through field-based studies of mantle peridotites hosted in high- and ultrahigh-pressure (HP-UHP) terrains. We review the case-study of the Ulten Zone peridotite lenses inside the eclogite-facies Variscan continental crust (Eastern Alps). These rocks record transition from spinel- (1200 °C; 1.5 GPa) to garnet-facies (850 °C; ~2.5 GPa) and represent mantle wedge tectonically emplaced in the subducted Variscan continental slab. Stability of amphibole and locally dolomite in the garnet-peridotites indicates modal metasomatism by C-O-H fluids. Radiometric constraints indicate that HP metamorphism of crust and garnet-bearing mantle rocks took place simultaneously at ~ 330 Ma.

Significant enrichment in Cs, Ba, Pb, U of the Ulten Zone garnet (+ amphibole ± dolomite) peridotites indicates that fluids were sourced by the associated crust and infiltrated the peridotites at HP, in a tectonic environment comparable to a slab-mantle wedge interface. Measurement of Fe³⁺ contents of garnet from Ulten Zone peridotites enabled to estimate oxygen fugacities (FMQ to FMQ +2) higher than those of garnet-peridotite xenoliths from sub-cratonic mantle, thereby indicating an oxidizing environment during fluid influx in the Ulten Zone mantle. Comparable features pertain to UHP mantle wedge rocks from Western Norway, suggesting that similar metasomatic processes potentially act on a large range of subduction depths. The Ulten Zone peridotites are thus relevant to assess the fluid-mediated crust-to-mantle element transfer during subduction, a major process for the chemical differentiation of the Earth.

Introduction

Garnet peridotites form a significant part of the Earth's upper mantle. Their occurrence as tectonic slivers inside high (HP) and ultrahigh-pressure (UHP) continental terrains implies that past events of subduction and plate collision caused the mechanical coupling of crust and mantle. This makes orogenic garnet peridotites relevant markers of deep dynamic processes allied with mountain building and plate convergence. In the last decade, an increasing number of work has shown that HP to UHP garnet peridotites may not belong to the lithospheric mantle of the subducted plates. Rather, they have been attributed to domains of the mantle wedge overlying the downgoing slab (Brueckner, 1998; Nimis and Morten 2000; Brueckner and Medaris 2000; Zhang *et al.*, 2000).

Figure 1. Tectonic sketch showing tectonic engagement of slices of mantle wedge inside the subducting continental crust.



Incorporation of large mantle "tectonic xenoliths" into the crust is also determined by density contrast between crust and mantle. Redrawn after Brueckner (1988).

Figure 1 shows that during subduction and buoyancy-driven exhumation of the continental crust, the top of the slab can incorporate slices of the overlying mantle either by tectonic erosion, or by density contrast (Brueckner, 1998). Once engaged in the crust, these large "tectonic mantle xenoliths" are carried to subcrustal levels and exhumed at the surface. Garnet peridotites from the Western Gneiss Region of Norway are examples of mantle wedge of such an origin, captured by the subducted Baltoscandian crust during the Caledonian orogeny (Beyer *et al.*, 2006; Lapen, 2009; Spengler *et al.*, 2009; Van Roermund 2009a). Moreover, several studies have documented that continental subduction can be traced to exceptional depths of 180-200 km, as suggested by the occurrence in UHP eclogites and gneiss of microdiamonds and of garnet with pyroxene exsolutions, derived from precursor majoritic garnet (Dobrzhinetskaya *et al.*, 1995; Sobolev and Shatzky, 1990; Ye *et al.*, 2000; Mposkos and Kostoupolos, 2001; Van Roermund 2009a). Slices of the overlying mantle wedge, as deep as 200 km can thus be trapped and carried to the surface to disclose information on major processes allied with mechanical coupling of crust and mantle during deep continental subduction (Scambelluri *et al.*, 2008; Spengler *et al.*, 2009). In addition, mantle wedge peridotites may preserve relicts of their history pre-dating the engagement in the crust, thus enabling a reconstruction of long term mantle dynamics (e.g. Nimis and Morten, 2000; Spengler *et al.*, 2006; Ye *et al.*, 2009, Van Roermund 2009b).

Petrologic and geochemical studies of orogenic garnet peridotites from HP and UHP settings have shown that these rocks can contain hydrous minerals (amphibole, phlogopite) associated with carbon-bearing phases (dolomite, magnesite, graphite/diamond) and can be enriched in incompatible elements and volatiles (Obata and Morten, 1987; Rampone and Morten, 2001; Van Roermund *et al.*, 2002; Zhang *et al.*, 2007; Sapienza *et al.*, 2009; Malaspina *et al.*, 2009a; Ye *et al.*, 2009). This reflects modal metasomatism due to interaction with agents released by the associated (underlying) subducted crustal slabs. HP and UHP orogenic garnet peridotites are thus proxies of deep fluid-mediated chemical exchange between crust and mantle. At subduction zones this exchange occurs over large scales and represents a major driving force to the chemical differentiation of the Earth. The geologic relevance of orogenic garnet peridotites has recently caused an increase in the scientific interest of these rocks,

especially if one considers that the chances to investigate deep Earth's mantle materials is quite limited. So far, knowledge on mantle wedge environments is mainly based on studies of peridotite xenoliths. These are essentially fist-sized samples hosted by lavas erupted in supra subduction settings: although providing first order information about the mantle in these regions, they represent limited rock volumes which can be affected by late stage reaction and chemical exchange with the host lava. Such xenoliths frequently contain metasomatic amphibole, phlogopite, pyroxene, carbonate (Vidal *et al.* 1989; Maury *et al.* 1992; Szabo *et al.* 1996; Laurora *et al.* 2001) and, occasionally, aqueous fluid or silicate glass inclusions with amphibole, phlogopite and locally carbonate daughter crystals (Trial *et al.* 1984; Mc Inness and Cameron, 1994; Schiano *et al.* 1995; Andersen and Neumann 2001; Demeny *et al.*, 2004; Ducea *et al.*, 2005). Most of these xenoliths are spinel-facies peridotites from the shallow mantle, roughly corresponding to fore-arc depths: interactions between subduction fluids/melts and mantle rocks at sub-arc and deeper levels have been poorly constrained so far. Different from xenoliths, the orogenic garnet peridotites form up to kilometre-scale mappable bodies preserving long-lived structural and petrologic histories and are potential witnesses of the deep tectonic and geochemical interplay between subducting plates and overlying lithospheric and asthenospheric mantle.

We will illustrate this concept presenting the textures and composition of the orogenic peridotites from the Ulten Zone (Eastern Italian Alps). They were part of a Variscan mantle wedge tectonically coupled with eclogitized continental crust (Nimis and Morten, 2000; Tumiatei *et al.* 2003). In the Ulten Zone peridotites, anhydrous spinel-facies assemblages are partly replaced by HP garnet + amphibole \pm dolomite parageneses as the result of cooling at increasing pressure and infiltration of slab fluids at eclogite-facies conditions (Obata and Morten 1987; Rampone and Morten, 2001; Scambelluri *et al.*, 2006).

The main focus of this paper is to provide an extensive review on the following major aspects of the Ulten Zone peridotites: (1) fluid infiltration at eclogite-facies conditions with formation of hydrous and carbonated parageneses in the garnet-facies stability; (2) the mineralogical and geochemical imprint produced by the crust-derived metasomatic agents in the mantle rocks; (3) the redox state of these peridotites during slab fluid infiltration

and the possible speciation of the incoming fluid phase. These features are finally compared with those of UHP mantle rocks from Western Norway (Bardane locality) crystallized at subduction depth of about 200 km. We show that in both cases the mantle wedge peridotites were flushed and metasomatized by incompatible element-enriched C-O-H fluids released by the subducted crust. Fluid presence or absence, respectively, determined rock recrystallization and/or preservation of former structures and compositions. Also, the metasomatic imprint imparted to these mantle rocks requires an involvement of the continental crust in deep subduction. We finally discuss the possible processes acting along a 100-200 km depth window during subduction.

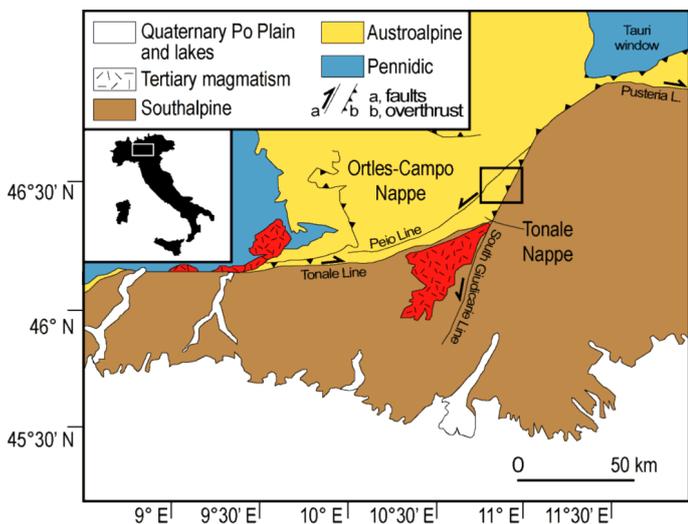
Geological background of the Ulten Zone and evolution of crustal rocks

Some of the best exposures of fresh garnet peridotites in the Eastern Alps outcrop is in an area located about 40 km west of Bolzano (Fig. 2), on the mountain range (Le Maddalene) that divides the upper Non valley (Val di Non, or Nonsberg) from the Ulten valley (Val d'Ultimo, or Ultental). This area, known as Nonsberg, or Ultental, or Ulten (zone or unit, hereafter Ulten Zone), is part of the Upper Austroalpine domain and has been the subject of intensive geological research (see Martin *et al.*, 1998; Morten *et al.*, 2004 for reviews). The Upper Austroalpine system consists of a metasedimentary cover and upper-to-lower crustal slices derived from the Mesozoic passive margin of the Adria microplate (Dal Piaz, 1993). According to Flügel (1990) and Neubauer and von Raumer (1993), the Austroalpine system of the Eastern Alps represents a remnant of the Variscan belt. North of the Tonale and Giudicarie lines, the Austroalpine system comprises a northern, cover-bearing nappe (Ortler nappe) and a southern, overlying, cover-free nappe (Tonale nappe) (Thöni, 1981).

The Ulten Zone belongs to the Tonale nappe that is separated to the North from the Ortler nappe by the Late Cretaceous Peio Line (Andreatta, 1948). To the south, the Giudicarie Line (a segment of the Periadriatic fault system) tectonically divides the Tonale nappe from the Southalpine domain. The Tonale nappe is subdivided into Tonale and Ulten Zones, which are divided by the Val Clapa and Rumo Lines (Morten *et al.*, 1976-1977). The Tonale Zone is mainly composed of sillimanite-bearing metasediments, metagranitoids with subordinated

marbles, calc-silicates and mafic layers affected by retro-grade Variscan metamorphism. In addition, an Alpine greenschist-facies overprint locally affects these rocks (Thöni, 1981).

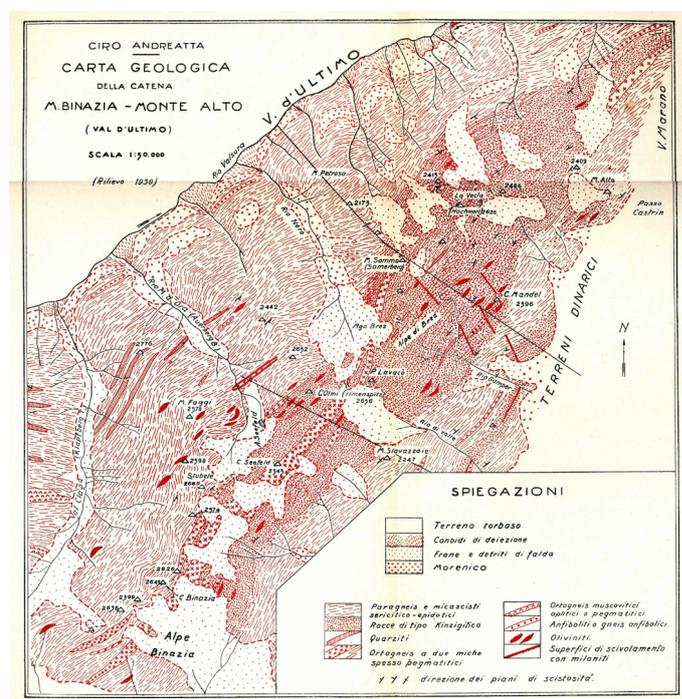
Figure 2. Geological sketch of the Central-Eastern Italian Alps and localization of the Ulten Zone (square).



The Ulten Zone is known as a site of interest for mineral collectors since the mid-nineteenth century (Doblicka, 1852). Before the XXth century, the Ulten Zone was the subject of intense field and petrographic works (Sandberger, 1866; Stache, 1880-1891; Ploner, 1881; Hammer, 1899). A major advance in geological knowledge of the UZ was provided by Andreatta in 1936 who published the geological and structural map (Fig. 3) that already reported the major gneiss and kinzigite that compose the Ulten Zone basement, and showed the metre- to hundred meters-long peridotite bodies (in full red, named olivinita) disposed along a major structural arrangement. Since 1970, several studies marked a new interest on the Ulten Zone basement (Amthauer *et al.*, 1971; Brenneis, 1971; Morten *et al.*, 1976; Herzberg *et al.*, 1977; Rost and Brenneis, 1978, see also the historical review by Tumiatì and Martin, 2003) and culminated into the paper by Obata and Morten (1987) that provided the first modern petrologic account on the spinel- to garnet-facies transition of the Ulten Zone peridotites and the metasomatic reactions governing the formation of garnet-amphibole peridotite. The crustal Ulten Zone lithologies have been successively subdivided into migmatites, garnet-kyanite gneisses and subordinate metagranitoids: an updated map is shown in Figure 4. The barrel-shaped ultramafic lenses

have been subdivided into spinel and amphibole-bearing garnet peridotites: these have been recognized to be located between the garnet-kyanite gneiss and the overlying migmatites. Boudins of mafic amphibolites and rare retrogressed eclogites also occur as lenses in the gneiss and migmatites. Different from the Tonale Zone, the Ulten Zone retains well-preserved Variscan high-pressure (eclogite to granulite facies) metamorphic structures and assemblages, only weakly overprinted by Alpine metamorphism (Obata and Morten, 1987; Martin *et al.*, 1994; Godard *et al.*, 1996).

Figure 3. Geological map of the Ulten Zone.

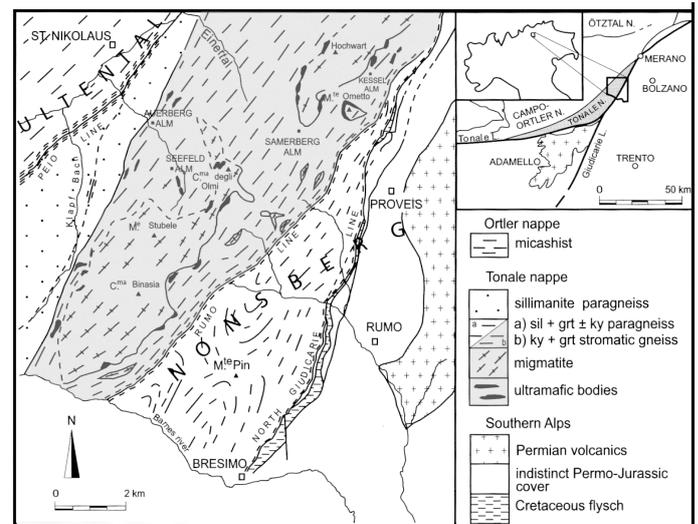


Drawn by Andreatta (1936).

The Ulten zone gneisses and migmatites are strongly foliated (Fig. 5A). The gneisses show mylonitic textures (Martin *et al.*, 1994, 1998; Godard *et al.*, 1996) and are composed by mm- to cm-sized bands of alternating layers with garnet + kyanite + biotite + rutile (Fig. 5B) and with quartz + plagioclase ± K-feldspar, transposed along an early (S1) mylonitic foliation. Such banded structure derive from S1 deformation of former melanosomes and leucosomes related to a pre-S1 partial melting event (Godard *et al.*, 1996). The gneisses grade upward into stromatic and nebulitic migmatites, which mostly show the mineral assemblage quartz + plagioclase + muscovite + biotite + garnet ± kyanite. Strongly residual layers in

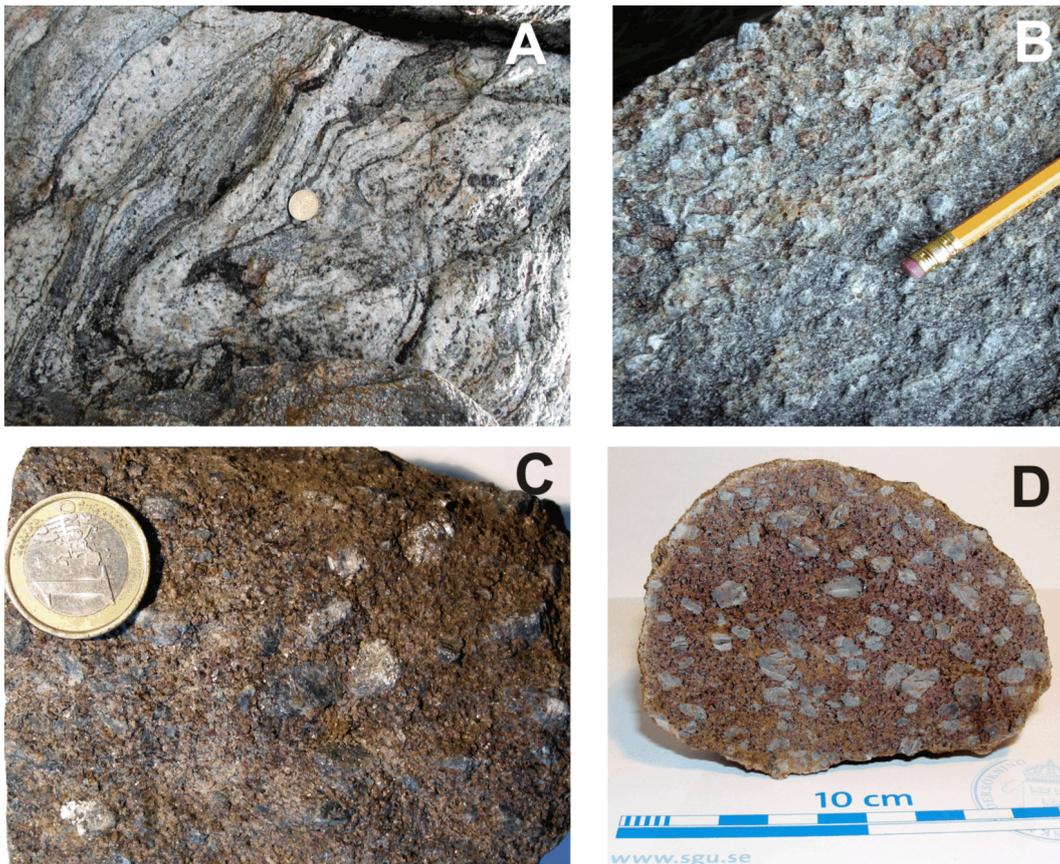
the gneiss and migmatite domains are almost entirely made of garnet + kyanite (rocks named ultenite, Fig. 5C, D): coexistence of garnet and kyanite in the restitic layers is strong indication that the early partial melting event(s) took place at depth during evolution of the Ulten Zone basement. In the least migmatized domains, amphibolized mafic lenses still preserve the relicts of a former eclogite paragenesis (Benciolini and Poli, 1993; Hauzenberger *et al.*, 1996; Godard *et al.*, 1996; Del Moro *et al.*, 1999). The migmatites and the enclosed peridotites are cut by trondhjemitic veins (plagioclase ± quartz ± biotite; Martin *et al.*, 1994, 1998; Godard *et al.*, 1996), which have been interpreted as the product of crystallization of calcalkaline deep-crust partial melts mixed with in-situ melts (Del Moro *et al.*, 1999).

Figure 4. Geological map of the Ulten Zone area.



Modified after Del Moro *et al.*, 1999.

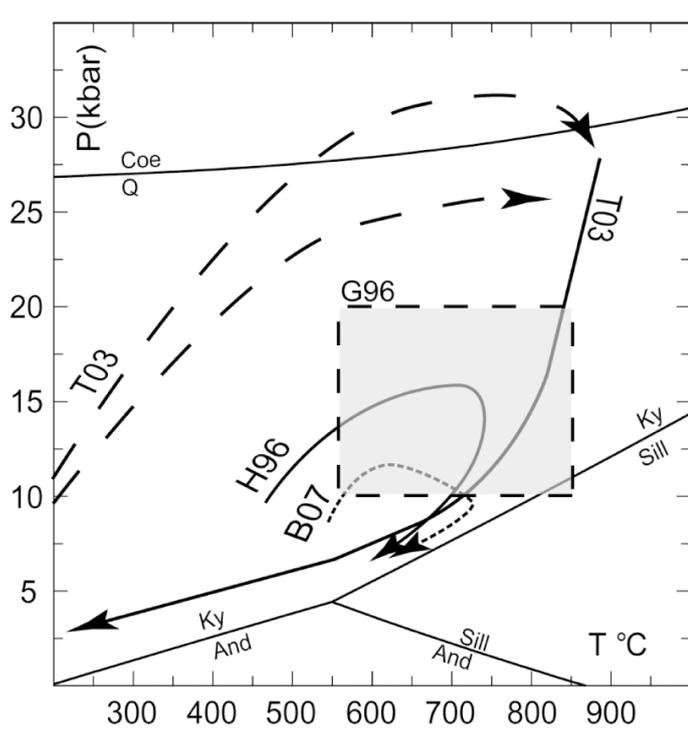
Figure 5. Migmatites and gneiss from the crustal Ulten Zone unit.



A: migmatite. B: garnet kyanite gneiss. C: garnet kyanite residue (Ultenite) after extraction of granitic melts at HP conditions. Blue kyanite porphyroblasts are in a matrix of dominant garnet grains D: cut surface of an Ultenite sample, showing the garnet porphyroblast, enclosing tiny garnet grains, and the garnet + oxide matrix.

The metamorphic-melting history of the Ulten Zone basement can be summarized as follows (Del Moro *et al.*, 1999): i) pre-S1 (Godard *et al.*, 1996) or syn-S1 (Hauzenberger *et al.* 1996) migmatization by dehydration melting; ii) S1 mylonitic deformation at eclogite-facies conditions; iii) post-S1 injection by exotic melts and further migmatization at eclogite-granulite conditions during decompressional uplift; iv) S2 shearing and retrogression.

Figure 6. Summary of available pressure-temperature paths reconstructed for the Ulten Zone crust.



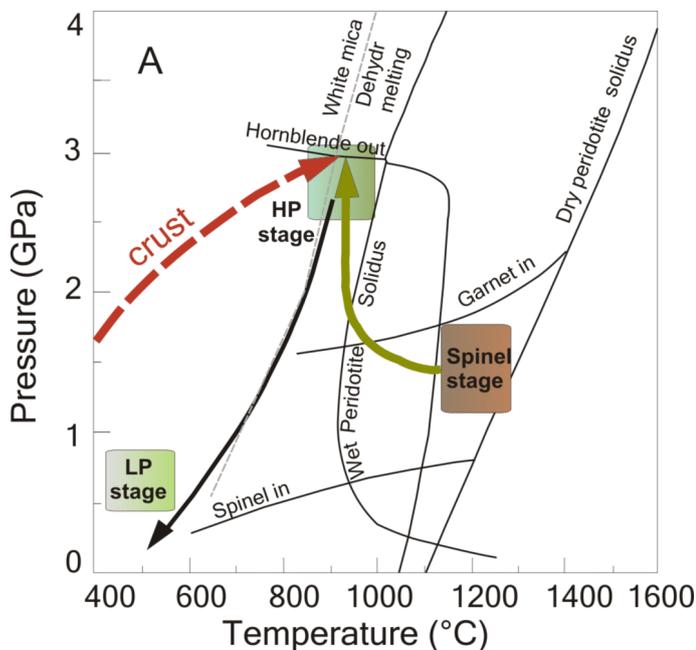
Modified from Braga and Massonne (2008), T03 Tumiati *et al.* (2003), G96 Godard *et al.* (1996), H96 Hauzenberger *et al.* (1996), B07 Braga *et al.* (2007). The quartz-coesite transition and the stability of the Al_2SiO_5 polymorphs have been calculated using PEPLEX (Connolly, 2005) and version 5.5 of the Holland and Powell (1998) thermodynamic data set.

In the Ulten Zone crust, thermobarometry of the peak high-pressure stage is hampered by extensive retrogression during uplift and post-S1 migmatization. The available estimates define a metamorphic evolution characterized by a clockwise P-T path, with a HP peak followed by thermal relaxation up to maximum temperature and, finally, retrogression under amphibolite- to greenschist-facies conditions. A summary of P-T paths drawn so far for the Ulten crustal rocks is reported in Figure 6. Using multi-equilibrium geothermobarometry, Godard *et al.*

(1996) calculated P-T conditions of 1.0-2.0 GPa, 600-900 °C for the garnet-kyanite gneisses. The large spread of P-T data depends on different assumptions on the water activity (X_{H_2O}) in the fluid phase occurring during the metamorphic evolution. In the same study, Godard *et al.* (1996) estimated pressure conditions below 1 GPa for the migmatites. Based on cation exchange and net-transfer geothermobarometry coupled with multi-equilibrium calculations, Hauzenberger *et al.* (1996) suggested a metamorphic peak of at least 1.5 GPa and 750°C. According to Tumiati *et al.* (2003), the prograde metamorphic evolution of the Ulten Zone crust reached a pressure peak near or within the coesite stability field (> 2.5 GPa, $T \approx 800^\circ\text{C}$), and eclogites and gneisses experienced peak high-pressure conditions similar to those of garnet peridotites. Mineral inclusions in large kyanite porphyroblasts along with calculated P-T pseudosections presented by Braga *et al.* (2007) allowed reconstruction of a complete P-T path characterized by a prograde epidote-amphibole-facies stage (P-T ≈ 0.85 GPa, 600 °C), a pressure peak at about 1.1-1.2 GPa and a subsequent temperature increase up to ~ 750 °C. Braga and Massonne (2008) suggested that the occurrence of P-T paths characterized by different peak conditions in a single tectonic unit may be the result of incomplete HP re-equilibration of large crustal blocks or, alternatively, the tectonic assemblage of crustal slivers suffering different P-T paths and finally amalgamated within a subduction channel. Ranalli *et al.* (2005) modelled the retrograde metamorphic evolution of the Ulten crust as a two-stage process. First, a near-isothermal decompression P-T path brought the crustal and mantle rocks association to mid-crustal levels (P = 0.7 GPa and T ~ 500 °C) in late Variscan times (~ 300 Ma), constrained on the basis of Rb-Sr white-mica geochronology (Hauzenberger *et al.*, 1993). Subsequently, the Ulten Zone basement underwent a slow decompression cooling path that ended in Permian-Jurassic times as indicated by Rb-Sr ages of biotite (Del Moro *et al.*, 1999). Sm-Nd dating of peridotites, country migmatites and eclogites yielded late Variscan (about 330 Ma) garnet-whole rock and garnet-clinopyroxene ages (Tumiati *et al.* 2003). These converging ages have suggested to Tumiati *et al.* (2003) that crystallization of the HP garnet peridotites, partial melting and eclogitization of crustal rocks took place simultaneously at eclogite-facies, and points to coupling of crust and mantle during subduction. The possible crust-mantle coupling

based on this reconstruction is reported in Figure 7. After this event, all lithologies underwent exhumation along a common retrograde *P-T* path (Godard *et al.*, 1996; Tumiat *et al.*, 2003).

Figure 7. *P-T* evolution of Ulten crust and mantle after Nimis and Morten (2001), Tumiat *et al.* (2003).



Green path refers to the mantle rocks, the red path refers to the subducted crust and the black path refers to the common exhumation of mantle and crust coupled together at eclogite-facies conditions.

Petrology of the Ulten Zone peridotites

The Ulten Zone peridotites outcrop as lenses (up to 10 m thick, tens to hundreds meters long) of harzburgite, lherzolite and minor dunite intruded by pyroxenite veins (Fig. 8A). They form a discontinuous horizon broadly located between underlying weakly migmatized foliated garnet + kyanite-bearing gneisses, and overlying migmatites (Godard *et al.*, 1996). When present, the peridotite banding and/or foliation is roughly concordant to the main planar anisotropy of the host rocks. The contacts between peridotite bodies and country gneiss are generally poorly exposed and often obscured by young faults; when exposed they are generally sharp and are locally marked by the development of hybrid $Phl \pm Amph \pm Chl$ -bearing layers (Godard *et al.*, 1996; Tumiat *et al.*, 2003, 2007; Marocchi *et al.*, 2007, 2010). The petrographic features of peridotites and pyroxenites have been described by Morten and Obata (1983) and Obata and Morten

(1987); further details have been reported by Godard *et al.* (1996), Nimis and Morten (2000), Godard and Martin (2000), Rampone and Morten (2001), Tumiat *et al.* (2003), Tumiat and Martin (2003), Morten and Trommsdorff (2003), Tumiat *et al.* (2007), Scambelluri *et al.* (2006), Sapienza *et al.* (2009). Here we present a summary of major textural characteristics of these rocks.

The Ulten Zone peridotites record a polyphase metamorphic history that is documented by the transformation of coarse (up to a few cm-sized crystals) spinel-bearing lherzolites (coarse-type) to fine-grained (0.2-1 mm-sized crystals) mylonitic peridotite varieties dominated by garnet + amphibole-bearing assemblages (fine-type). The latter largely prevails over the coarse-type. The garnet + amphibole peridotites are locally associated with garnet + amphibole + dolomite-peridotites: carbonate-bearing and carbonate-free rocks occur in the same and/or in nearby outcrops (Sapienza *et al.*, 2009). Pyroxenite veins record a similar evolution from very coarse (≤ 6 cm) clinopyroxenites to fine-grained garnet + amphibole \pm olivine-bearing websterites (Morten and Obata, 1983; Nimis and Morten, 2000).

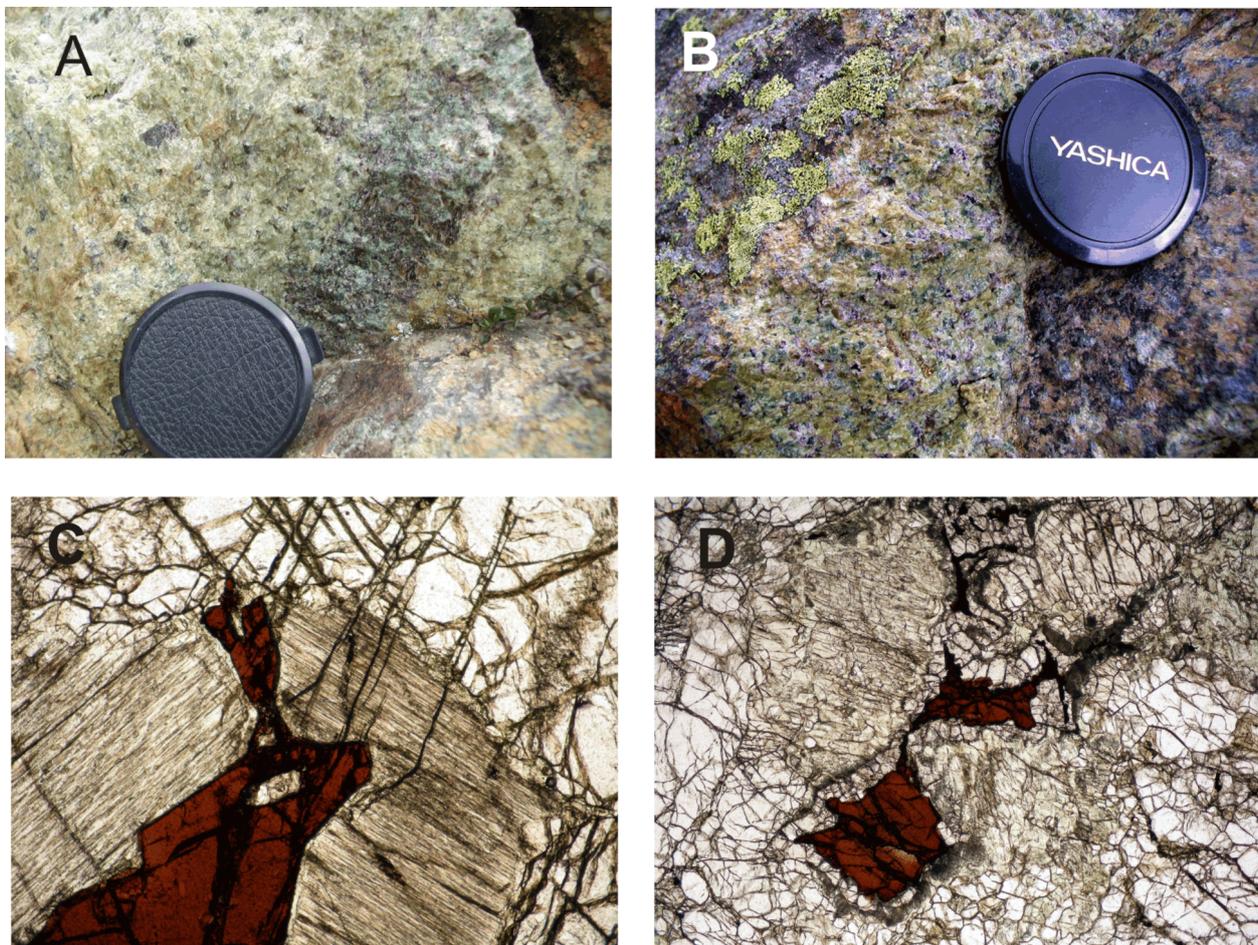
Coarse spinel-facies peridotites with coronitic garnet

The coarse spinel peridotites are restricted to weakly deformed domains within some peridotite bodies. They preserve protogranular textures (Fig. 8B) and display olivine, ortho, clinopyroxene and spinel showing equilibrium textures. Amphibole is absent within the above spinel-facies assemblage and occurs as secondary phase along the pyroxene grain boundaries. Thermobarometry of the spinel lherzolites yields $\sim 1200^\circ\text{C}$ and 1.3-1.6 GPa. $T \geq 1400^\circ\text{C}$ and comparable pressures have been obtained for the early crystallization of the associated pyroxenites (Nimis and Morten, 2000). In the coarse spinel-bearing peridotites, garnet occurs in reaction coronas around spinel (Fig. 8B, C) and in granoblastic aggregates in equilibrium with neoblastic pyroxene and olivine. Coarse ortho- and clino-pyroxene in these rock varieties show along cleavages complex exsolutions and/or replacement textures made of pyroxene, garnet, amphibole and subordinated spinel along cleavages (Godard *et al.*, 1996). In some samples, neoblastic edenitic-pargasitic amphibole occurs in the fine-grained granoblastic garnet-bearing domains; these domains can additionally contain dolomite and apatite, to form a stable assemblage with olivine, orthopyroxene, amphibole and garnet. The garnet assemblages developed by cooling to $\sim 850^\circ\text{C}$ and *P*

increase to ~2.7 GPa of the spinel peridotites (Fig. 6; Nimis and Morten, 2000). Maximum pressure and temperature estimates are also provided by the presence of amphibole and dolomite in the garnet bearing assemblage. These two minerals in peridotite systems can survive up to maximum pressures of 3 GPa (for amphibole, Fumagalli and Poli, 2005) and 2 GPa for dolomite at temperatures of 900 °C (Tumiati *et al.*, 2009). The coexistence of amphibole and dolomite has been experimentally determined for KNCFMAS + C-O-H systems up to 1.8 GPa and 900-1000 °C (Tumiati *et al.*, 2009). Maximum temperatures for dolomite stability are provided by the carbonate solidus located at 930-1080 °C and a pressure

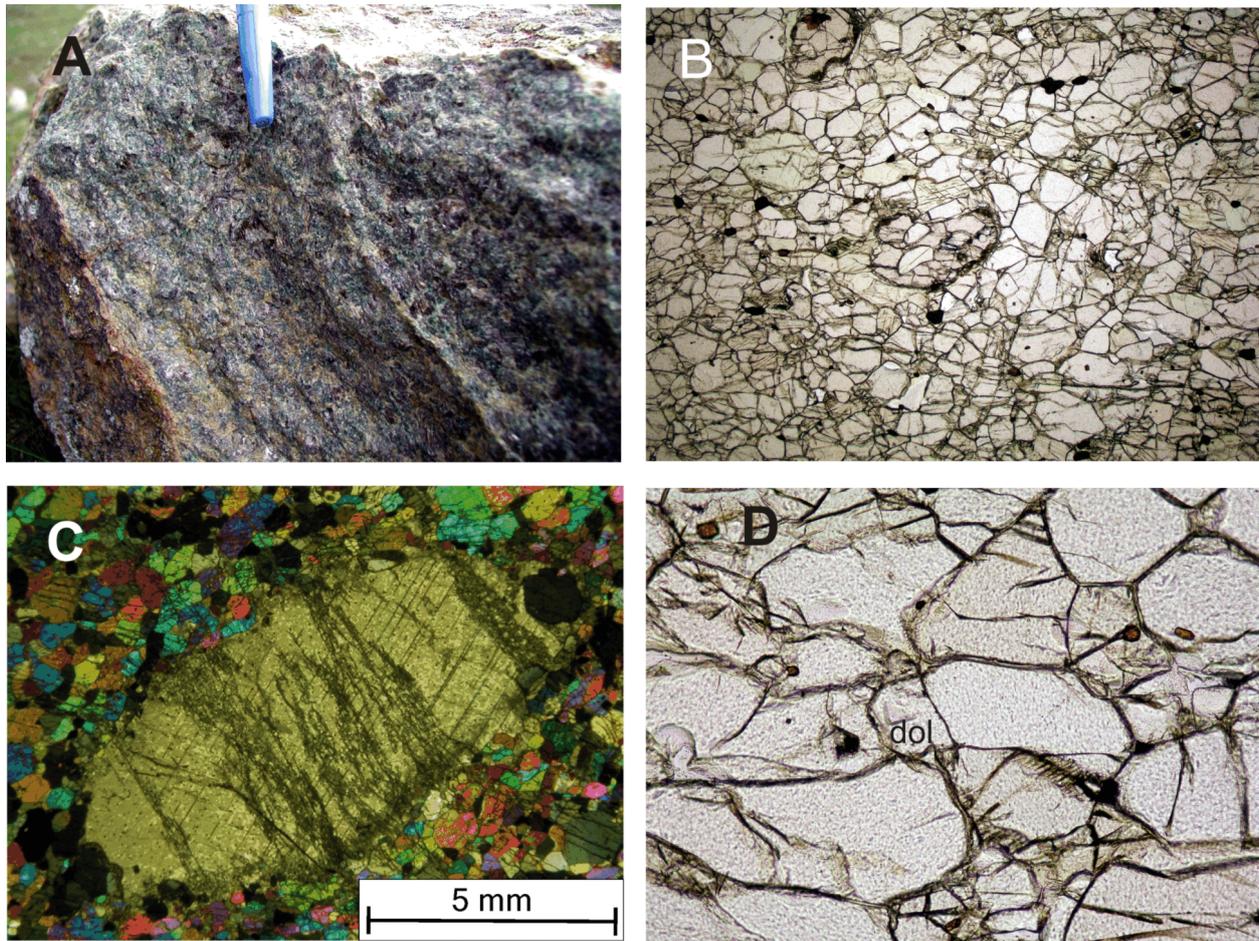
range of 2.1-3 GPa for hawaiian pyrolite compositions (Wallace and Green, 1988) or at 1060 and 2.6 GPa for KNCFMAS + C-O-H systems (Tumiati *et al.*, 2009). Using the experimental data of Wallace and Green (1988), Sapienza *et al.* (2009) determined maximum 2.5 GPa and 850 °C, for crystallization of the garnet + amphibole + dolomite assemblage in the carbonated garnet peridotites of the Ulten Zone.

Figure 8. Meso- and micro-structures of coarse spinel-facies peridotites with coronitic garnet.



A: pyroxenite vein inside the spinel peridotite. B: spinel peridotite with coronitic garnet. The black crystals in the peridotite are spinel grains, pink garnet forms clear corona textures around spinel. C: transmitted light photomicrograph of a spinel peridotite with fresh unreacted spinel grains (brown; about 1 mm long) showing equilibrium texture with exsolved orthopyroxene. The coarse white mineral at the top right corner is olivine. D: transmitted light photomicrograph of spinel grains (brown; 0.5 mm long) with garnet coronas. They are surrounded by coarse exsolved clinopyroxene (pale green), orthopyroxene and olivine (white coarse mineral in the lower half of the picture).

Figure 9. Meso and microstructures of mylonitic (garnet + amphibole ± dolomite) peridotites.



A: mylonitic (garnet + amphibole) peridotite. The main foliation dips from left to right side of the photograph. It consists of amphibole and finegrained garnet associated with olivine, clino and orthopyroxene. B: transmitted light photomicrograph of the mylonitic foliation, with stable garnet (pink crystal at the centre of the picture), amphibole (pale green), olivine (white), clino and orthopyroxene. Image width is 5 mm. C: transmitted light photomicrograph (crossed nicols) of a dolomite porphyroclast surrounded by apatite grains and showing internal recrystallization along microfractures. The porphyroclast is set in a fine-grained matrix of (garnet + amphibole)-harzburgite composition. D: transmitted light photomicrograph of a dolomite neoblast in the matrix. Foliation is defined by the preferred orientation of elongated amphibole.

Mylonitic garnet + amphibole ± dolomite peridotites

Widespread shearing, hydration and sinkinematic recrystallization during the high-pressure stage produced fine-grained peridotites characterized by dominant tabular to mosaic granular textures (Fig. 9). These rocks mostly consist of granoblastic olivine + orthopyroxene + garnet + amphibole aggregates, with minor or no clinopyroxene and rare dolomite, phlogopite and apatite (Obata and Morten, 1987). Transition from coarse to fine types is testified by porphyroclastic garnet-bearing samples. In the fine-type, amphibole is modally abundant (13-23 vol %) and ranges in composition from pargasite-edenite cores with up to 1 wt% K₂O to Mg-hornblende rims (Obata and Morten, 1987; Nimis and Morten, 2000;

Rampone and Morten, 2001; Tumiatì, 2002). Increase in modal amphibole is associated with progressive disappearance of clinopyroxene and, eventually, garnet as a response to increasing hydration (Obata and Morten, 1987). Hydration was locally accompanied by development of centimetre-sized veinlets of euhedral garnet plus pargasite-edenite, corresponding to zones of fluid influx (Tumiatì *et al.*, 2003). The mylonitic garnet + amphibole peridotite varieties are locally associated with dolomite-bearing peridotites. The carbonated peridotites contain millimetre- to centimetre-sized porphyroclasts of dolomite, garnet (enclosing relic spinel) and weakly zoned amphibole set in a finer-grained mylonitic matrix (< 1 mm sized). Dolomite porphyroclasts are about 1 cm in

size (Fig. 9c): they display fine-scale internal recrystallization along microfractures and are surrounded by apatite grains (up to 1.3 mm). A second generation of HP minerals occurs in the foliated matrix, which consists of olivine, orthopyroxene, elongated amphibole, garnet, dolomite and clinopyroxene (Fig. 9d). Modal estimates by Obata and Morten (1987) indicate that these samples may contain 72% olivine, 16% orthopyroxene, 3.4% amphibole, 7.9% garnet; clinopyroxene, dolomite and apatite are present in subordinate amounts. The occurrence of dolomite and apatite in the fine-grained garnet peridotite domains suggests their equilibrium crystallization at garnet-facies conditions. Mineral compositions and semiquantitative thermobarometry suggest that the mylonitic garnet + amphibole peridotites developed at roughly the same conditions as the coronitic garnet assemblages in the coarse peridotites (Obata and Morten, 1987; Tumiati *et al.*, 2003).

Retrogression of the garnet-bearing mineral assemblages is recorded by (i) mineral zoning (Nimis and Morten, 2000; Tumiati *et al.*, 2003), (ii) formation of symplectites (orthopyroxene + clinopyroxene + spinel and orthopyroxene + amphibole + spinel) after garnet (Godard and Martin, 2000), and (iii) complete garnet and clinopyroxene replacement of amphibole + spinel (Susini and Martin, 1996; Scambelluri *et al.*, 2006; Marocchi *et al.*, 2007). The retrograded peridotites rarely preserve relicts of garnet and pyroxene and generally consist of amphibole + orthopyroxene + olivine + spinel \pm phlogopite (modal amphibole content up to 20 vol%). Occasionally, a new REE(La)-epidote (dissakisite) occurs in fine-grained spinel + amphibole-bearing peridotite deriving from retrogression of former garnet-bearing peridotite (Tumiati *et al.*, 2005). Further retrogression produces olivine + tremolite + cummingtonite + chlorite + talc and widespread serpentinization. Peridotite lenses locally display reaction rims towards the contact with the host migmatized gneiss. These derive from peridotite-gneiss interaction either during exhumation of the crust-mantle association (Marocchi *et al.*, 2010) or, alternatively, during subduction (Tumiati *et al.*, 2007). These reaction zones are dm-thick bands, well exposed in the Mt. Hochwart area (northeastern Ulten Zone), which display a layered distribution of metasomatic minerals. From migmatite to peridotite the following zones can be distinguished (Marocchi *et al.*, 2010): phlogopite \pm tremolite \pm apatite \pm zircon (zone 1), tremolite + phlogopite + anthophyllite

(zone 2) and anthophyllite \pm chlorite \pm talc (zone 3). Locally, Mg-hornblende-rich domains with accessory Cl-rich Fe-kinoshitalite, a rare Ba-rich mica (Tumiati *et al.*, 2007). These hybrid reaction layers display very high contents of fluid-mobile elements, whereas Li is preferentially hosted by anthophyllite. The nature of the metasomatic aqueous fluids responsible for the crystallization of the metasomatic bands is debated. According to Marocchi *et al.* (2010) the reaction zone has been produced by infiltration of hydrous fluids at $T \approx 660\text{--}700\text{ }^{\circ}\text{C}$ and $P < 1.2\text{ GPa}$, during exhumation of coupled continental crust and mantle peridotites. Conversely, based on the occurrence of Cl-rich apatite and Cl-rich Fe-kinoshitalite in the reaction bands, Tumiati *et al.* (2007) proposed that metasomatic reactions were enhanced by deep infiltration of ocean water in the subduction channel.

The geochemical fingerprint of the Ulten Zone garnet-bearing peridotites: record of crustal metasomatism by subduction fluid

The major and trace element composition of the Ulten Zone peridotites has been the subject of several papers that contributed to build a large and complete dataset (Obata and Morten, 1987; Morten and Obata, 1990; Rampone and Morten, 2001; Scambelluri *et al.*, 2006; Tumiati *et al.*, 2007; Marocchi *et al.*, 2007, 2010; Sapienza *et al.*, 2009). We refer to the above contributions for details and tables with analytical results. In terms of most major and trace elements (Si, Mg, Ca, Al, Sc, Co, V, Ni), no systematic correlation exists between bulk peridotite compositions, textural types (coarse vs. fine) and metamorphic assemblage (spinel vs. garnet + amphibole; Morten and Obata, 1990; Bondi *et al.*, 1992). Variations in element concentrations most likely reflect primary heterogeneities of the mantle protoliths. The fine-grained (garnet + amphibole) types are significantly enriched in alkalis (especially K_2O) and Large Ion Lileophile Elements (LILE): this enrichment is unrelated to major element chemistry and is roughly correlated with the Sr isotopic compositions of the peridotites (Bondi *et al.*, 1992; Petrini and Morten, 1993; Rampone and Morten, 2001).

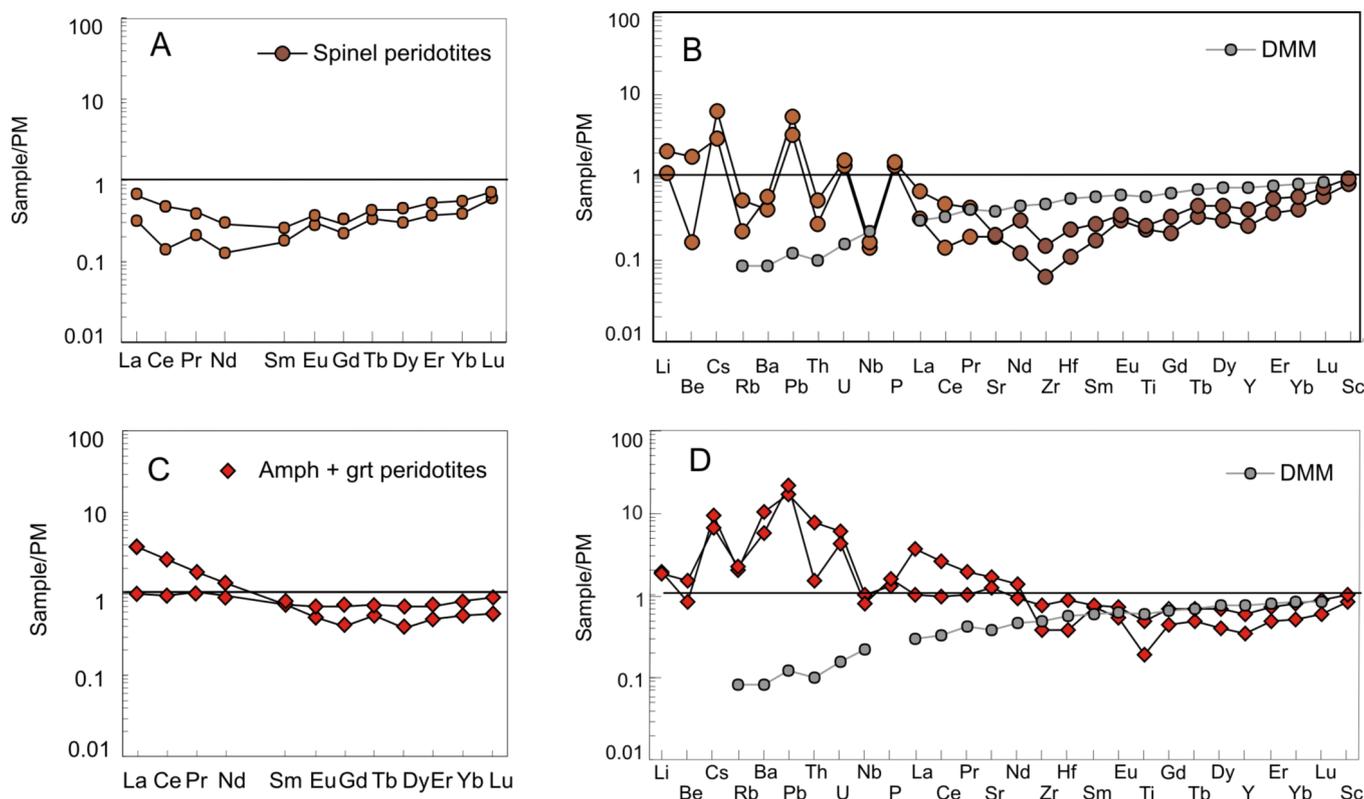
Hereafter we present separately the main bulk-rock and mineral chemistry features of the coarse spinel- and of fine-grained (garnet + amphibole)- bearing peridotites.

Bulk rock compositions.

The spidergrams in Figure 10 report the REE and the other trace element compositions of spinel (Fig. 10A, B) and (garnet + amphibole) peridotites (Fig. 10C, D) normalized to the Primitive Mantle (Mc Donough and Sun, 1995). All samples display decreasing heavy REE (HREE) with decreasing atomic number, a common feature of depleted peridotites that is in agreement with the

variability of Al_2O_3 , CaO, MgO and indicates that the starting peridotites recorded variable degrees of depletion (Rampone and Morten 2001). For this reason they are compared in Figure 10 to a depleted mantle source (DMM, Workman and Hart, 2005).

Figure 10. Bulk-rock REE and trace element samples.



Bulk-rock REE (left side) and trace element (right side) compositions of spinel peridotites (A and B) and of (garnet + amphibole ± dolomite) peridotite samples (C and D). Normalization to Primitive Mantle by McDonough and Sun (1995)

The spinel peridotites of Figure 10A, B did not recrystallize to garnet-facies assemblages (i.e. they do not contain appreciable modal garnet and amphibole): they have low REE abundances, below 1 x PM and U-shaped REE patterns variably enriched in LREE. Comparable features pertain to samples with coronitic garnet, scarcely affected by garnet + amphibole crystallization (see Rampone and Morten, 2001).

The (garnet + amphibole) peridotites (Fig. 10C, D) display REE abundances around the PM: they have flat HREE to MREE spectra and LREE enrichments up to 10 x PM. As outlined by Rampone and Morten (2001), this variability is unrelated with the degree of major element

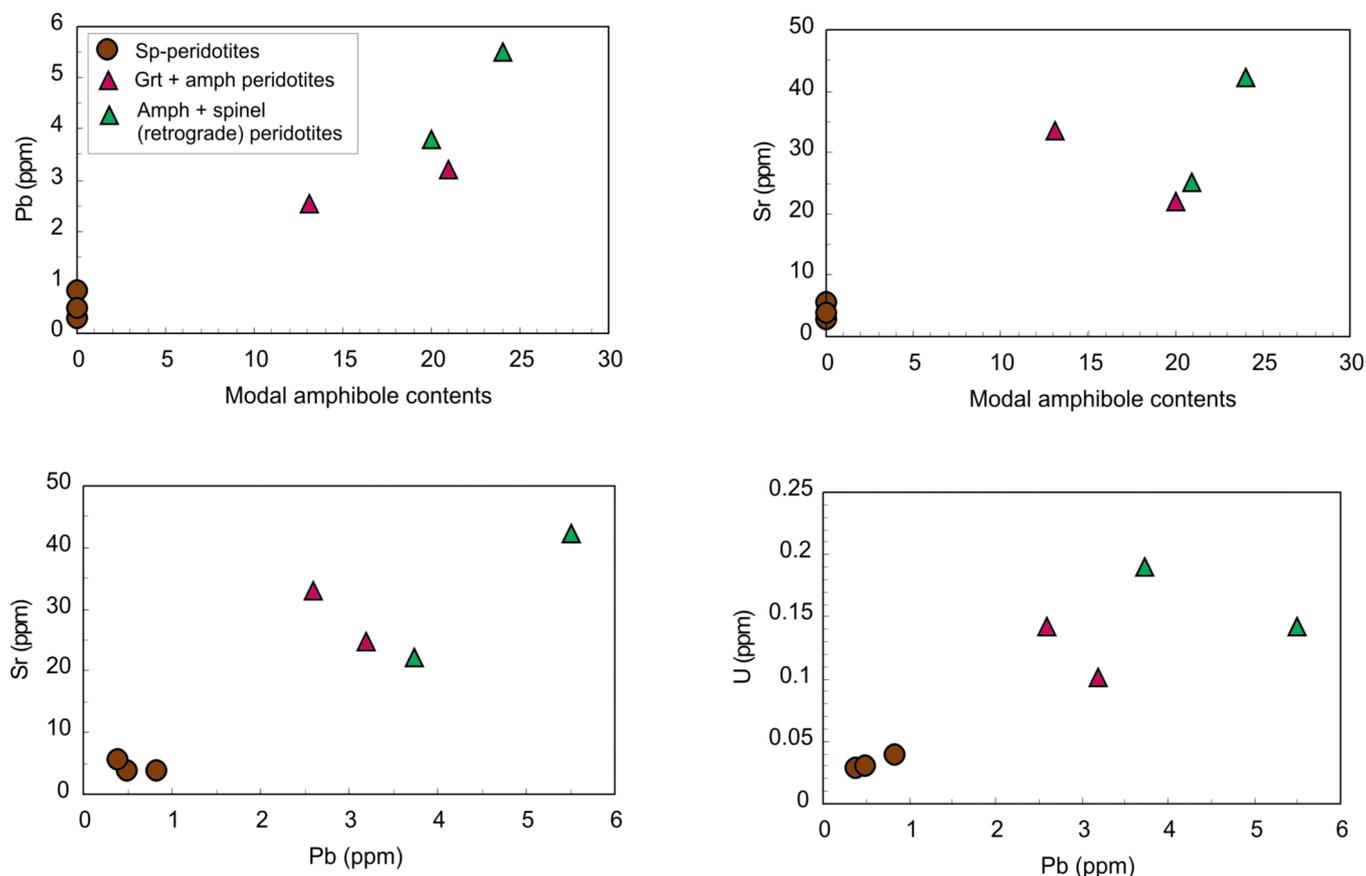
depletion. Figure 10 shows that the amphibole-free spinel peridotites and the garnet + amphibole peridotites are all affected, although in different extent, by metasomatic LREE enrichment.

The trace element spidergrams (right hand side of Fig. 10) show that all samples, spinel-peridotites included, display positive anomalies in LILE, particularly Cs, Pb and U. This occurs irrespective of the depletion in Al_2O_3 and CaO and the degree of enrichment is significant if compared with the DMM (e.g. Rb, Ba, Th, P in spinel peridotites). The (garnet + amphibole) peridotites display higher Rb, Ba, Th than the spinel peridotites. Lithium is appreciably enriched (about 2 x PM) in the majority of

the peridotite samples analysed (Scambelluri *et al.*, 2006). The selected samples are affected by minor serpentinization and by formation of small modal amounts of retrograde tremolitic amphibole; hence some incompatible element enrichment (e.g. Li, Cs, Ba, Rb) can be in principle attributed to retrograde metamorphism. Some of the above mentioned incompatible elements display positive correlations with the modal amphibole contents (estimates from Rampone and Morten 2001). As an example, the bulk-rock Pb and Sr versus modal amphibole diagrams (Fig. 11) illustrate the coupled increase in such elements and water in the amphibole-bearing peridotites.

Positive correlation trends are also defined by the incompatible element pairs Pb–Sr and Pb–U (Fig. 8). This indicates that the transition from dry spinel lherzolites to wet (amphibole ± garnet) peridotites was assisted by the influx of an aqueous fluid carrying incompatible trace elements. The early timing of this event (peak eclogitic or retrograde) can be fixed by measuring the trace element compositions of specific mineral assemblages.

Figure 11. Bulk-rock variability of several fluid-mobile elements.



Mineral compositions

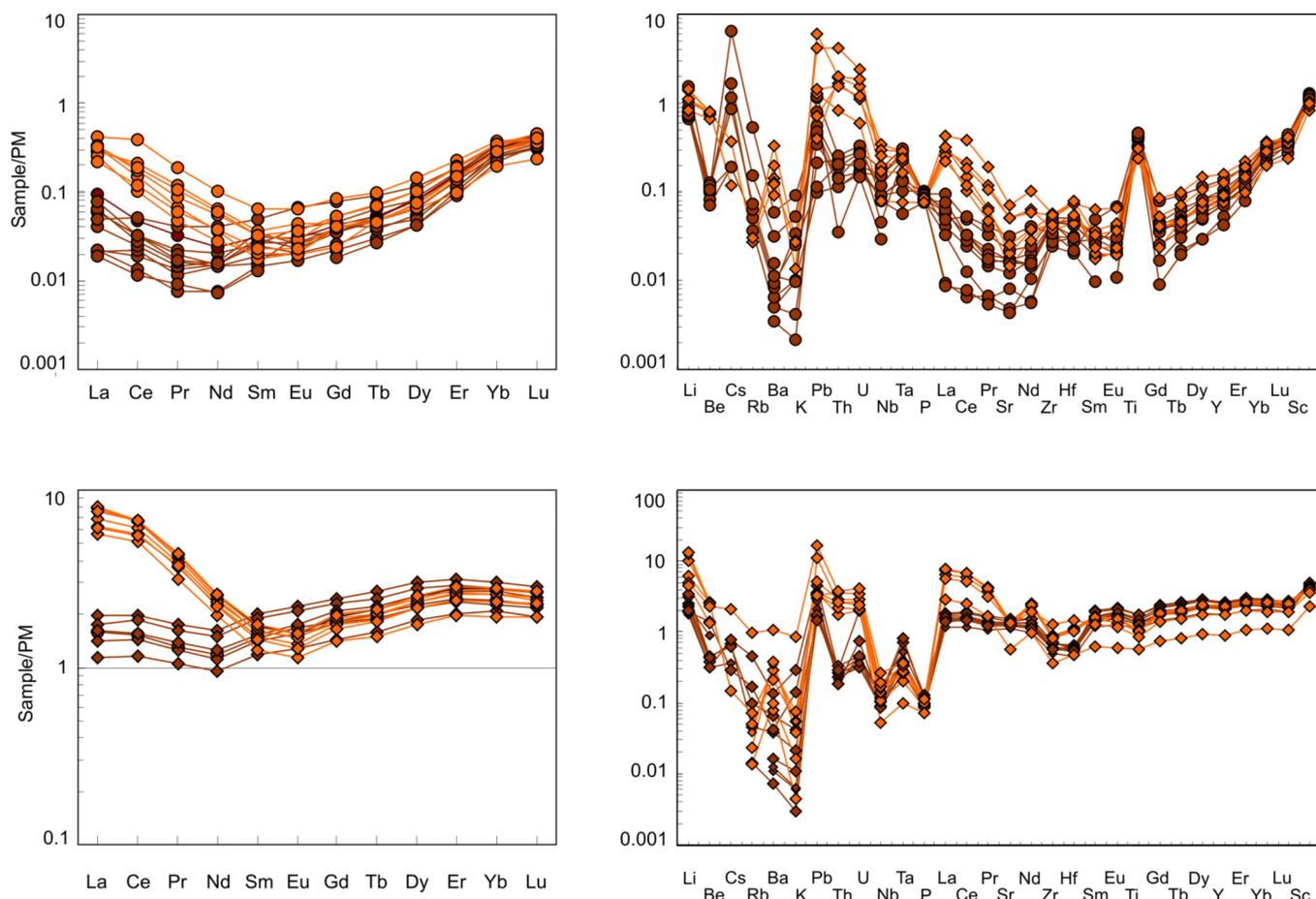
The average compositions of minerals from the spinel-peridotites are shown in the PM-normalized diagrams of Figure 12. Clino- and ortho-pyroxene from these rocks have convex-upwards REE patterns, depleted in MREE and variably enriched in LREE. Both ortho- and clinopyroxene enriched in LILE with respect to high field strength elements (HFSE), with normalized Pb/Nb

ratio in clinopyroxene (representing the LILE/HFSE fractionation) ranging from 16 to 90. The LREE- and LILE-enriched trace element signature of spinel facies pyroxenes indicates that the spinel peridotites experienced a cryptic metasomatism by chromatographic porous flow (Bodinier *et al.*, 1990) that likely predated subduction zone metasomatism and fluid infiltration during garnet-facies recrystallization and coupling with the crust

(Scambelluri *et al.*, 2006). This metasomatism has been ascribed by Scambelluri *et al.* (2006) to high-temperature interaction with subduction-related siliceous melts when

these mantle rocks were at relatively shallow (spinel-facies) lithospheric depths.

Figure 12. Rare earth element and trace element compositions



Rare earth element and trace element compositions of orthopyroxene (A and B) and of clinopyroxene (C and D) from two spinel peridotite samples, reported with two different colours (brown and orange) in the figure. Normalization as in Figure 5.

The compositions of the main rock-forming minerals in the garnet peridotites are shown in Fig. 13. These rocks contain garnet, clinopyroxene, orthopyroxene, olivine, amphibole (\pm phlogopite, carbonate and apatite) in textural equilibrium and represent highly deformed, hydrated and locally carbonated mantle rocks. The LREE content of the garnet-facies clinopyroxene is up to 10 x PM (Fig. 13); the coexisting orthopyroxene is slightly enriched in LREE. Compared with the spinel-facies pyroxenes, they display much lower HREE, between 0.1 and 0.01 x PM, monitoring full equilibration with garnet at eclogite-facies. Amphibole in textural equilibrium with garnet has LREE-enriched patterns (La up to 10–30 PM) and low HREE contents (0.3–0.5 PM). More generally,

the garnet-facies amphibole has flat HREE, about 2 x PM: this suggests partial HREE re-equilibration of amphibole during retrograde garnet breakdown. Clinopyroxene in the (amphibole + garnet) peridotites is enriched in Li, Be, Cs, Ba, Pb, U. It also displays high Pb_N/Nb_N (330–615) and low Ce_N/Pb_N (1.39–2.66) ratios, compared with the spinel-facies clinopyroxenes. Olivine has Li and P between 3–4.5 ppm and 40–70 ppm, respectively. Dolomite has $LREE/HREE \gg 1$ (La_N/Yb_N up to 317); the PM-normalized incompatible multi-element diagram shows enrichments in Ba, Pb and Sr over U, Th, REE and HFSE; the latter are often below detection limits or they occur in very low concentrations (e.g. Hf < 0.01 ppm, Nb < 0.085 ppm, Ta < 0.01 ppm).

HREE depleted amphibole coexisting with garnet (see Fig. 13) indicates that peridotite hydration occurred at eclogite-facies conditions. This demonstrates that water-rich fluids entered the anhydrous spinel-facies peridotites during subduction-related high-pressure metamorphism. Relevant features of the (garnet + amphibole) peridotites are the bulk-rock positive anomalies in Cs, Ba, Pb, U and Li (twice the PM; Fig. 13). The LILE and LREE budget is nearly entirely hosted by amphibole and clearly reflects addition of crust-derived components to the mantle rocks. Therefore, the coupled increase of modal amphibole content (see Fig. 11) and bulk Sr, Pb, U was achieved during fluid-mediated eclogitization of the mantle wedge Ulten Zone peridotite.

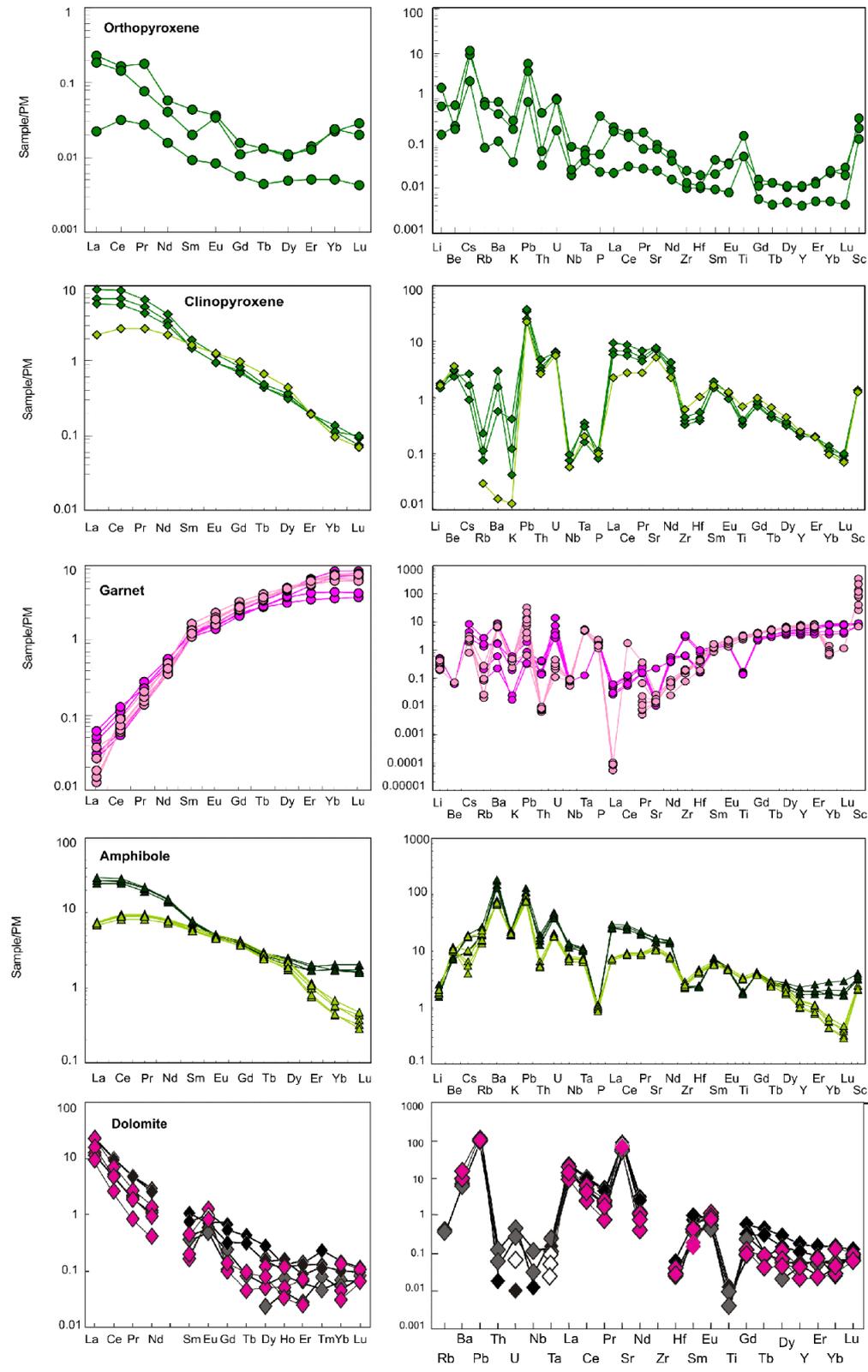
Amphibole in the Ulten garnet peridotites exhibits high LILE and relatively low HFSE content (Fig. 13). Amphibole and phlogopite are common minerals in metasomatized mantle rocks and provide important information about the nature and composition of metasomatic agents. Amphibole related to alkali-rich silicate melts is generally LILE- and HFSE-enriched and does not display fractionation between these elements (Ionov *et al.*, 1993). Selective enrichment in LILE with respect to HFSE, as shown by the garnet-bearing Ulten Zone peridotites, is documented in mantle xenoliths affected by carbonatite metasomatism and in orogenic peridotites infiltrated by crust-derived metasomatic agents (Zanetti *et al.*, 1999; Malaspina *et al.*, 2006; Scambelluri *et al.*, 2008). In the Finero peridotite, for instance, LILE-enriched and HFSE-depleted amphibole has been linked to mantle wedge metasomatism by Si-rich hydrous melts (Zanetti *et al.*, 1999). Comparable geochemical fingerprints in amphibole from sub-arc peridotite xenoliths have been either ascribed to hydrous fluids (Vidal *et al.*, 1989; Maury *et al.*, 1992), or to hydrous melts (Schiano *et al.*, 1995). Based on the above arguments, on bulk-rock compositions and on the increasing modal amount of amphibole at the expense of pyroxene, the garnet-facies Ulten Zone amphibole has been attributed to infiltration of crust-derived aqueous fluids (Rampone and Morten, 2001; Scambelluri *et al.*, 2006).

The presence of dolomite in some high-pressure Ulten garnet-peridotites is known since the early work of Morten and Obata (1987) and witnesses the presence and local saturation of CO₂ in the metasomatic fluid (Rampone and Morten, 2001). Sapienza *et al.* (2009) have shown that the Ulten Zone carbonated garnet peridotites display

stable dolomite + apatite in HP garnet-bearing subduction assemblage, as shown by the texture and by the HREE depleted composition of dolomite (Fig. 13). Similarly to the associated clinopyroxene and amphibole, dolomite is also enriched in MREE to LREE. It thus appears that amphibole and apatite play a major role as trace element repositories, although dolomite is a major host for Sr, Ba, Pb and, subordinately, LREE. As shown by Sapienza *et al.* (2009) the trace element compositions of the garnet-facies clinopyroxenes and amphiboles from dolomite-free and dolomite-bearing Ulten Zone rocks largely overlap. Since these peridotite varieties constitute the same (or nearby) outcrops and have been closely associated in space and time, they record infiltration of a common metasomatic CO₂-H₂O fluid with low CO₂/H₂O. Water consumption from the fluid during amphibole crystallization led to CO₂ saturation in the fluid and to dolomite formation (Rampone and Morten 2001). Low CO₂/H₂O ratio in the metasomatic Ulten Zone fluid is also suggested by the experimental constraints on fluid phase mobility in the mantle. Watson *et al.* (1990) determined low wetting angles (60°) for CO₂-rich fluids at mantle depths, which favour their stagnation in isolated pockets and prevent their mobility along interconnected networks. On the other hand, aqueous fluid may occur as an interconnected mobile phase at P = 3 GPa and T approaching the solidus.

Peridotite reaction with carbonate-rich melts can produce metasomatic effects (Ionov and Harmer 2002) comparable with the ones described for the Ulten dolomite peridotites. However, several evidence are inconsistent with a melt-related origin of the Ulten Zone carbonate-bearing assemblages. Sapienza *et al.* (2009) have shown that during metamorphism of the Ulten Zone peridotites, carbonate melts are unstable and should crystallize and/or quench, thus producing carbonate pockets and veins as described in mantle xenoliths (e.g. Ducea *et al.* 2005; Ionov *et al.* 1996). Reaction of such melts with peridotites also produces abundant clinopyroxene. These features are not observed in the Ulten Zone peridotites, where modal clinopyroxene decreases as the result of progressive addition of water-rich fluids (Morten and Obata, 1987; Rampone and Morten, 2001). Based on these evidence, Sapienza *et al.* (2009) proposed that the dominant metasomatic phase affecting both the dolomite-free and the dolomite-bearing Ulten peridotites was a water-rich, CO₂-bearing fluid.

Figure 13. Rare earth element and trace element compositions



Rare earth element and trace element compositions of minerals of the (amphibole + garnet + dolomite) peridotite. Normalization as in Figure 5.

The pressure–temperature conditions attained during peak eclogite-facies metamorphism by the Ulten Zone dolomite-bearing peridotites are essentially the same as those recorded by the dolomite-free (garnet + amphibole) peridotites (Sapienza *et al.*, 2009). Based on experiments on the peridotite–CO₂–H₂O system (Wallace and Green, 1988), Sapienza *et al.* (2009) proposed that crystallization of the Ulten(garnet + dolomite) peridotites occurred at subsolidus conditions (1.8–2.5 GPa and T < 950°C) in the presence of H₂O and C-bearing fluid phases. This estimate is consistent with: (1) the 2.5 GPa P estimate based on the Na₂O contents of amphiboles in the HP assemblage (up to 2.5 wt% Na₂O; Obata and Morten 1987; Niida and Green 1999) and (2) the amphibole stability in peridotite–H₂O systems (Fumagalli and Poli, 2005). Carbonatite melts coexisting with (amphibole + garnet) peridotites form above 950 °C in a 2.1 - 3.1 GPa range, whereas C-bearing silicate melts form at higher temperature (Wallace and Green 1988). The Ulten Zone (garnet + amphibole + dolomite) peridotites can be viewed as potential sources of carbonic melts in a subduction setting: their protracted subduction to higher P-T conditions is a possible mechanism leading these rocks to partial melting and release of carbonatite and/or carbon-bearing silicate melts to the mantle wedge (Sapienza *et al.*, 2009). Carbonated and hydrated (phlogopite-bearing) garnet peridotites like the ones from Ulten can represent metasomatized mantle potentially able to generate ultrapotassic magmas like those erupted in the Roman and Lucanian Magmatic Italian Provinces. An increasing number of papers has recently related formation of these magmas to partial melting of lithospheric upper mantle metasomatized by sedimentary-carbonate components derived from the subducted slab. (Conticelli *et al.* 2002; D'Orazio *et al.* 2007; Avanzinelli *et al.* 2008, 2009; Frezzotti *et al.*, 2009)

The redox state of Ulten Zone peridotites and inference on fluid phase speciation

Crystallization of amphibole and dolomite in the HP Ulten garnet peridotites due to influx of aqueous-carbonic fluids makes these rocks a relevant natural laboratory to understand C and volatile recycling in the mantle via subduction. This represents the "missing link" of global volatile cycles due to inaccessibility of subduction environments. Also, unravelling "how" C-O-H compounds occur in the mantle, i.e. their speciation, is necessary to

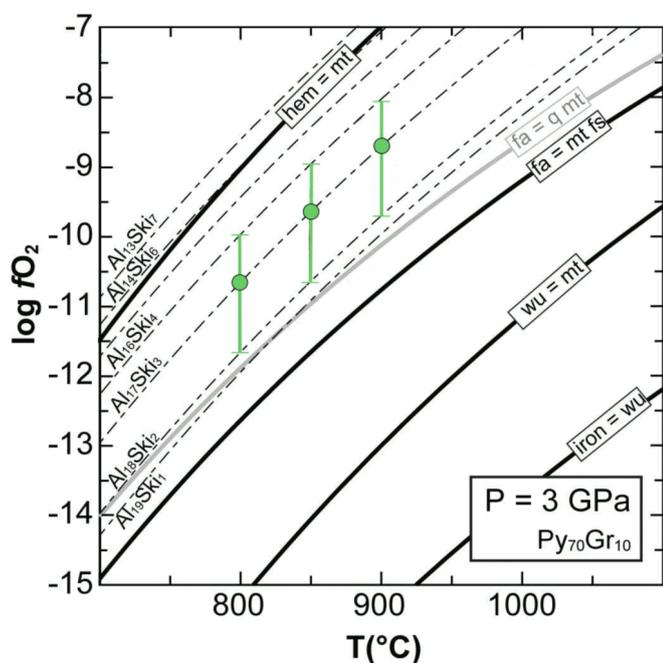
predict the evolution of carbon species during long-term geochemical cycles. Natural mineral assemblages and laboratory experiments demonstrate that the composition of C-O-H fluids in the mantle closely relates to the oxidation state of the system (Van Roermund *et al.*, 2002; Carswell and Van Roermund, 2005; Scambelluri *et al.*, 2008; Tumiati *et al.*, 2009; Malaspina *et al.*, 2009b; Malaspina *et al.*, 2010). The latter issue is relevant for C recycling, as either diamond/graphite generally crystallize depending on the chemical potential of oxygen and therefore on the oxygen fugacity. Graphite and diamond generally behave as refractory phases, whereas carbonates, although refractory, are highly reactive (Canil, 1990). An estimate of oxygen fugacity (fO_2) attained by the Ulten Zone garnet (+ amphibole + dolomite)-bearing peridotites is thus essential to model C transfer during subduction.

The equilibria between ferric (Fe³⁺) and ferrous (Fe²⁺) iron in mineral assemblages buffer the oxygen fugacity and the C-O-H fluid speciation. On the other hand, the C-O-H species in fluids or melts can control the oxidation state of mantle phase assemblages by redox processes (Luth, 1999). Being the Fe³⁺/Fe²⁺ equilibria of mantle parageneses and the speciation of C-O-H fluids so related, Malaspina *et al.* (2009b) determined the iron oxidation state of garnet in the Ulten Zone peridotites. Several redox equilibria involve Fe³⁺-garnet components; for an olivine-orthopyroxene-Fe³⁺-garnet assemblage, one of these reactions is:

(1) $2 \text{Fe}^{2+}_3\text{Fe}^{3+}_2\text{Si}_3\text{O}_{12}$ (skiaigite) = $4 \text{Fe}^{2+}_2\text{SiO}_4$ (fayalite) + $2 \text{Fe}^{2+}_2\text{Si}_2\text{O}_6$ (ferrosilite) + O₂ where the ferric garnet component "skiaigite" contains both Fe³⁺ and Fe²⁺ (Luth *et al.*, 1990; Gudmundsson and Wood, 1995; Woodland and Peltonen, 1999). The electron microprobe analysis of the Fe³⁺ content of garnet from the Ulten peridotite (equivalent to skiaigite substitution for almandine) adopting the "flank method" (Höfer and Brey, 2007; see details in Malaspina *et al.*, 2009b) provided skiaigite contents in the order of 3 (±1) mol%. The corresponding fO_2 has been calculated by Malaspina *et al.* (2009b) using the Perple_X software (Connolly, 1990) applying the redox equilibrium (1) and integrating solid solution models for garnet (pyrope-grossular-almandine-skiaigite; Malaspina *et al.*, 2009b), olivine (forsterite-fayalite; Holland and Powell, 1998) and orthopyroxene (enstatite-ferrosilite; Holland and Powell, 1996). The resulting redox equilibria are shown in the isobaric T-log fO_2 section

computed at 3 GPa pressure (Fig. 14): the dashed curves represent the equilibria selected for pseudocompounds approaching the investigated mineral compositions (olivine = Fo89; orthopyroxene = En89; garnet = 70% pyrope, 10% grossular and variable skiaegite/almandine depending on oxygen fugacity). The equilibria involving hematite, magnetite, fayalite, quartz, ferrosilite, wustite and iron at various buffering conditions are also shown in Figure 14 (continuous lines) for comparison. The estimated oxygen fugacities range from -10.69 to -8.94 log units (Fig. 14); the resulting $\Delta \log fO_2$ [=log fO_2 (sample) - FMQ] range between zero and +2 (Fig.15).

Figure 14. Log fO_2 and speciation of a graphite-C-O-H fluid.



Log fO_2 (a) and speciation of a graphite-C-O-H fluid (b) calculated at 3 GPa and 850 °C as a function of $X(O) = n_O/(n_O+n_H)$. The green line (a) and dashed green area (b) is the fO_2 range calculated for the Ulten peridotites. Calculation have been performed with the programme "species" in Perplex package (Connolly, 1995). FMQ = fayalite-magnetite-quartz buffer, WM = wustite-magnetite buffer, IW = iron-wustite buffer.

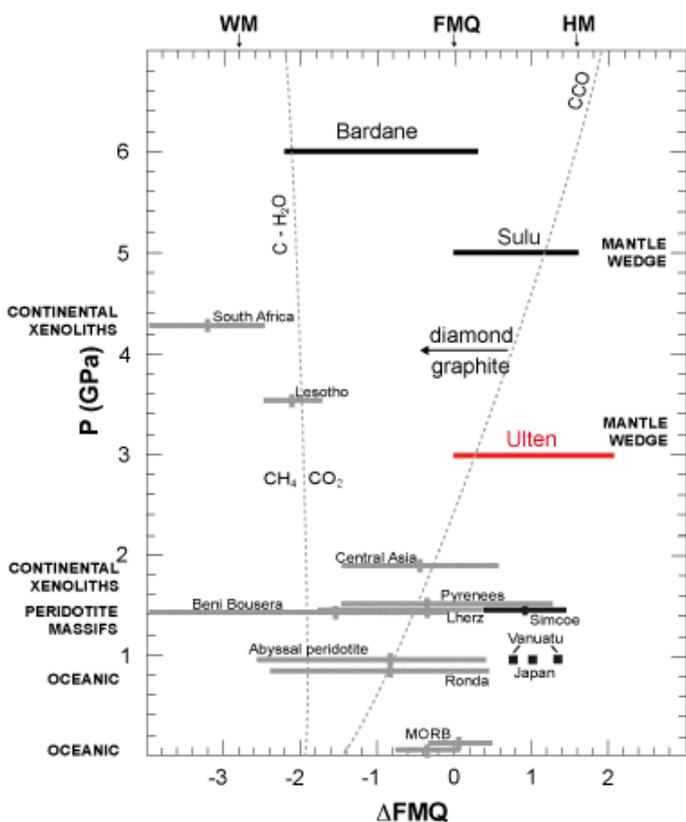
In Figure 15, the estimated oxygen fugacities of the Ulten Zone garnet peridotites (expressed as $\Delta \log fO_2$ values) are plotted as a function of P, together with other mantle peridotites from distinct geological environments. Measured fO_2 values vary from: (i) 1 to 3 log units below the FMQ in abyssal peridotites (Bryndzia & Wood,

1990); (ii) $\Delta \log fO_2 = +1$ to -2 for peridotite massifs, with samples from Beni Bousera reaching up to $\Delta \log fO_2 = -4$ (Woodland *et al.*, 1992; Woodland *et al.*, 2006); (iii) $\Delta \log fO_2 = -1$ to $+2$ for spinel peridotites from subcontinental lithospheric mantle, with significant heterogeneities (Wood *et al.*, 1990; Canil *et al.*, 1990; Brandon and Draper, 1996; Parkinson and Arculus, 1999). The garnet peridotites from sub-cratonic mantle have the lowest fO_2 values, below $\Delta \log fO_2 = -2$ (Woodland and Koch, 2003). Differently from these mantle rocks, the Ulten peridotites display high $\Delta \log fO_2$ values (0 to +2). These values are comparable with those estimated for spinel peridotite xenoliths from subduction settings (Simcoe, Vanatu and Japan; $\Delta \log fO_2$ between -1 and $+1.5$; Brandon & Draper, 1996; Parkinson *et al.*, 2003). Importantly similarly high values of fO_2 are shown by other UHP orogenic garnet peridotites, like the ones from Sulu (China) (Malaspina *et al.*, 2009b; Malaspina *et al.*, 2010). These data point to a lateral oxygen fugacity variation related to different tectonic settings (e.g. Woodland and Koch, 2003; Frost and McCammon, 2008).

As previously mentioned, the fO_2 recorded by the Ulten peridotites have implications on the speciation of the coexisting C-O-H fluid phase. According to Holloway and Reese (1974) and to the model of Connolly (1995), C-saturated fluids can be either methane-bearing or carbon-dioxide bearing as a function of the oxygen fugacity imposed by the redox conditions of the system. At high pressures H_2O is the dominant species in the C-O-H fluid, which will be a mixture of CH_4 - H_2O at lower fO_2 and of H_2O - CO_2 at higher fO_2 . Despite the absence of diamond and graphite in the studied peridotites, a C-saturated system can be used as a proxy to estimate the fluid composition. This is possible because at the high pressure and temperature conditions attained by the Ulten Zone garnet-peridotites, the graphite saturation boundary approaches the binary joins H_2O - CO_2 and H_2O - CH_4 (Holloway & Reese, 1974). Based on this reasoning and on calculations performed using the GC-O-H-MRK equation of state by Connolly and Cesare (1993) for a C-saturated C-O-H fluid, Malaspina *et al.*, (2009) have evaluated the C-O-H molecular species concentrations of the metasomatic fluid. This points to high water content of the fluid and the presence of CO_2 (instead of CH_4) at $\Delta \log fO_2 > 0$. This confirms the expectations of what discussed by Rampone and Morten (2001) and Sapienza *et al.* (2009)

on the basis of petrographic evidence and trace element budgets.

Figure 15. Δ FMQ versus pressure.



Range and average value of oxygen fugacities relative to FMQ ($\Delta \log fO_2 = \log fO_2 \text{ sample} - \log fO_2 \text{ FMQ}$) for the Ulten garnet peridotites (red line) plotted as a function of pressure (modified after Malaspina et al., 2009b). This is compared with selected examples of spinel and garnet peridotites from different tectonic settings, equilibrated at similar T conditions (~800-900 °C): oceanic mantle lithosphere (Bryndzia & Wood, 1990), peridotite massifs (Woodland et al., 1992; Woodland et al., 2006), garnet peridotite xenoliths from sub-cratonic mantle (Woodland and Koch, 2003) and mantle wedge from spinel facies (Brandon and Draper, 1996; Parkinson and Arculus, 1999; Peslier et al., 2002). Mantle wedge-derived orogenic garnet peridotites from Sulu (Eastern China) and Bardane (Western Gneiss Region) are also reported in black lines (Malaspina et al., 2009b, 2010). The CCO oxygen buffer ($C+O_2 = CO_2$) and the C-H₂O join ($X(O) = 1/3$) separating CH₄- and CO₂-rich aqueous fluid, calculated at 900 °C, are also portrayed in dashed lines.

Major implications and comparison with metasomatized mantle rocks from greater depths

The transition from spinel- to garnet-bearing assemblages in the Ulten peridotites enables to trace the evolution of this mantle from shallow regions towards deeper and cooler levels of the wedge flushed by subduction fluids (Fig. 15). Nimis and Morten (2000) and Scambelluri et al. (2006) proposed location of the starting spinel-peridotites in a relatively hot domain above an asthenospheric melt source. The Pb, U, Li enrichment of the Ulten Zone anhydrous spinel-peridotites can be suggestive of exchange with a (subduction-related?) melt phase enriched in crustal components. Scambelluri et al. (2006) proposed that the metasomatic imprint of the early spinel peridotites might have been acquired by interaction with melts produced during Variscan subduction (Fig. 15). However, this interpretation is hampered by a lack of age constraints for the pristine spinel-facies metasomatism, and it cannot be excluded that it was achieved during older (pre-Variscan?) events that caused the re-enrichment of this lithospheric mantle domain (Petrini and Morten, 1993).

Lateral corner-flow motion brought the spinel-peridotites towards the subducting slab into a P-T regime where fluids are released from slabs (Fig. 16) (Scambelluri and Philippot 2001; Manning 2004). Available studies on the Ulten Zone peridotites agree on the fact that garnet-facies crystallization was driven by aqueous subduction fluids sourced from the crustal rocks nearby (Rampone and Morten, 2001; Tumiati et al., 2003; Scambelluri et al., 2006; Sapienza et al., 2009). Sm-Nd ages of garnet-peridotites, country migmatites and eclogites indicate a common late Variscan (330 Ma) HP event of peridotite metasomatism and partial melting plus eclogitization of crustal rocks (Tumiati et al. 2003). The exact mechanism of peridotite metasomatism is still unclear. According to some authors, crystallization of the garnet-facies assemblage occurred when the spinel-facies rocks were tectonically sliced in the subducting slab (Nimis and Morten 2000; Rampone and Morten, 2001). Alternatively, Scambelluri et al. (2006) proposed that metasomatism occurred before engagement in the crust, when peridotites were still settled in the mantle above the slab (Fig. 16). At eclogite-facies, partial melting of the Ulten continental crust produced the migmatites locally in contact with the peridotite lenses. However, the metasomatic

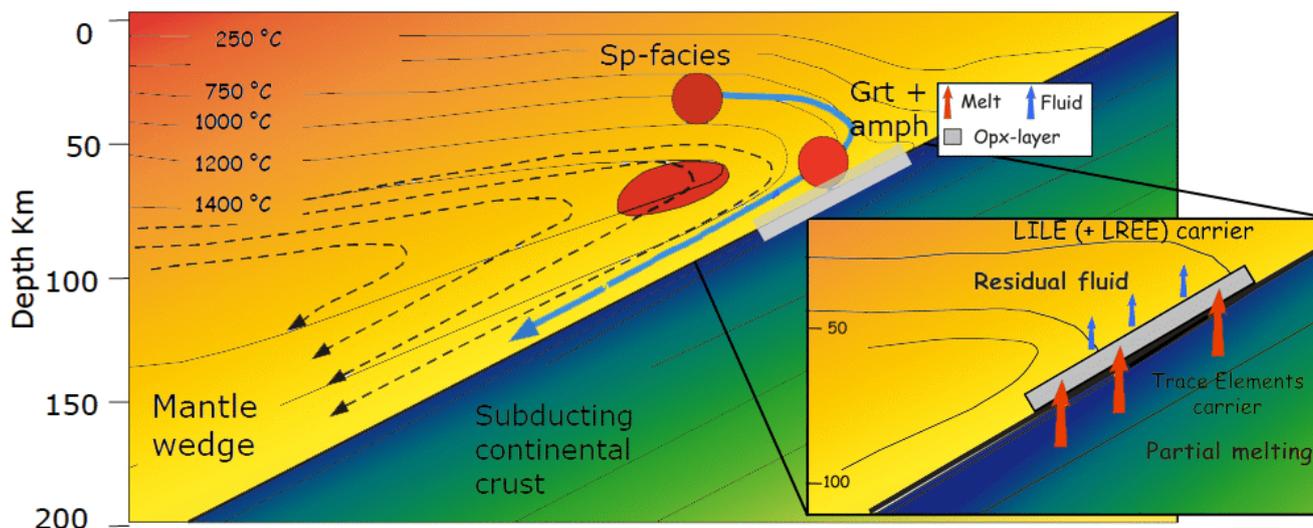
style of the (amphibole + garnet) peridotites indicates that the main agent was an aqueous fluid, not a siliceous melt, and lack of diffuse orthopyroxene overgrowths in these rocks provides compelling evidence that siliceous melt infiltration was not the dominant metasomatic process (Rampone and Morten, 2001). Rather, aqueous fluids have been individuated as dominant agent.

Two mechanisms have been proposed to explain the extraction of C-O-H fluids from the migmatized crustal slab. Rampone and Morten (2001) proposed that the C-O-H fluid responsible for amphibole and dolomite formation in the peridotites was released by the in situ crystallization of hydrous granitic melts produced by the associated crust. Another possible way of C-O-H fluid extraction from these melts requires their interaction with mantle peridotites, to produce pyroxenite reaction layers plus residual aqueous-carbonic fluid (Fig. 16; Scambelluri *et al.* 2006). Although pyroxenites are present in the Ulten Zone peridotites (Braga *et al.* 2007), reactive pyroxenite layers and siliceous melt/peridotite reaction zones with (ortho)pyroxene formation after olivine are not yet documented. Therefore there is no direct evidence of an orthopyroxene-rich reactive layer between crustal and mantle Ulten Zone rocks. Interaction between peridotite and siliceous subduction agents has been documented by studies on UHP rocks from Dabie-Shan (China; Malaspina *et al.*, 2006). In this setting, reaction between mantle peridotites and siliceous fluids/melts formed garnet-orthopyroxenite layers and released incompatible element-rich aqueous fluids able to migrate and metasomatize the overlying mantle wedge. The reactive behaviour at the subducted crust-mantle interface may thus filter the slab fluids to produce aqueous fluids enriched in the most incompatible and volatile components (C included) that ultimately flush the mantle. Crystallization of hydrous phases as amphibole or phlogopite may shift the fluid toward CO₂-rich compositions and enable carbonate crystallization in inner domains of the mantle wedge. In this second scenario, the reactive orthopyroxene horizon potentially occurring at the Ulten Zone has been tectonically deleted; in this case tectonic incorporation of peridotites into the country rock gneisses might have occurred after the major stage of metasomatism.

The Ulten orogenic mantle wedge peridotites are thus examples of fluid-mediated chemical exchange between subducted plates and overlying mantle. Comparison with other ultra-deep mantle wedge materials may help to

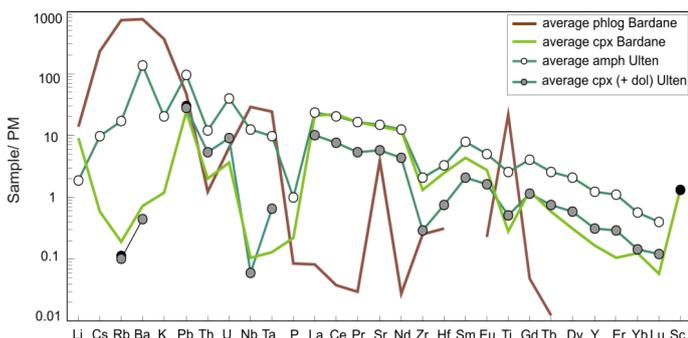
clarify the extent of crust-mantle exchange during subduction. In the following we compare the Ulten rocks with metasomatized UHP garnet websterites in the locality of Bardane (Fjørtoft island, W Norway), that contain orthopyroxene, clinopyroxene, garnet, phlogopite, dolomite/magnesite and locally showing microdiamond inclusions (Van Roermund *et al.*, 2002). The websterites are hosted by garnet peridotites which represent deep cratonic mantle formed in the Archean (Spengler *et al.*, 2006): these mantle rocks have been part of a wedge involved in Caledonian orogeny and tectonically coupled with the Baltoscandian continental crust during ultradeep subduction to 200 km depth (Scambelluri *et al.*, 2008; Spengler *et al.*, 2009; Van Roermund 2009a). During subduction fluids released from the continental crust flushed and metasomatized the Bardane mantle (Brueckner *et al.*, 2002, Van Roermund *et al.*, 2002; Carswell and Van Roermund 2005; Scambelluri *et al.*, 2008). Despite the difference in age, orogenic setting and crystallization depths, the mantle rocks from Bardane and Ulten share relevant geologic similarities as they: (1) are tectonically inserted in eclogitized HP and UHP continental rocks (Godard *et al.*, 1996; Dobrzhinetskaya *et al.*, 1995). (2) contain hydrates and carbonates in the HP and UHP parageneses, witnessing metasomatism due to influx of C-O-H fluids that reached carbonate saturation. Figure 17 reports the average trace element compositions of: (1) the Ulten HP clinopyroxene and amphibole, and (2) the Bardane UHP clinopyroxene and phlogopite. These represent the major trace element repositories in such rocks and the spidergram shows that clinopyroxenes from both settings have very similar patterns. The REE contents of the Bardane clinopyroxene are higher than those from Ulten: this can be explained by coexistence of the Ulten clinopyroxene with amphibole, which is a preferential LREE host and lowers the LREE budget of associated clinopyroxene. On the other hand, clinopyroxene in Bardane equilibrates with phlogopite which has low affinity for LREE: for this reason the Bardane clinopyroxene is the LREE sink. Clinopyroxene from Ulten and Bardane are similarly depleted in LILE compared with coexisting amphibole and phlogopite due to preferential LILE partitioning in the latter phases. The above discussed similarities in trace element patterns of clinopyroxenes suggest that the metasomatic agents infiltrating the mantle wedge rocks at Bardane and Ulten were compositionally similar.

Figure 16. General scenario for the Ulten peridotite evolution (after Nimis and Morten 2000).



Equilibration in the spinel facies field (above a melting mantle region represented by the red area below the spinel-facies field) is followed by peridotite hydration and crystallization to garnet + amphibole assemblages in a wedge setting above the subducting crust and/or during engagement in the crust. These stages are followed by exhumation (redrawn from Scambelluri et al., 2006).

Figure 17. Comparison of the trace element compositions.



Comparison of the trace element compositions of the major trace element mineral repositories from the peak assemblages in Bardane (clinopyroxene and phlogopite, green and brown continuous lines, respectively) and Ulten Zone (clinopyroxene and amphibole, grey and white dots, respectively). Normalization as in figure 5.

As shown in Figure 15, the Bardane peridotites exhibit lower fO_2 values relative to the Ulten peridotites. As a consequence, such a high oxygen fugacity recorded by the Ulten peridotites inhibited carbon precipitation from the CO_2 -bearing metasomatic fluid (as evidenced by the location of the CCO equilibrium in Figure 15). More generally, the mantle wedge Ulten, Sulu and Bardane peridotites record a systematic decrease of fO_2 with depth: this trend is similar to the one defined by subcratonic mantle xenoliths (e.g. Central Asia, Lesotho and

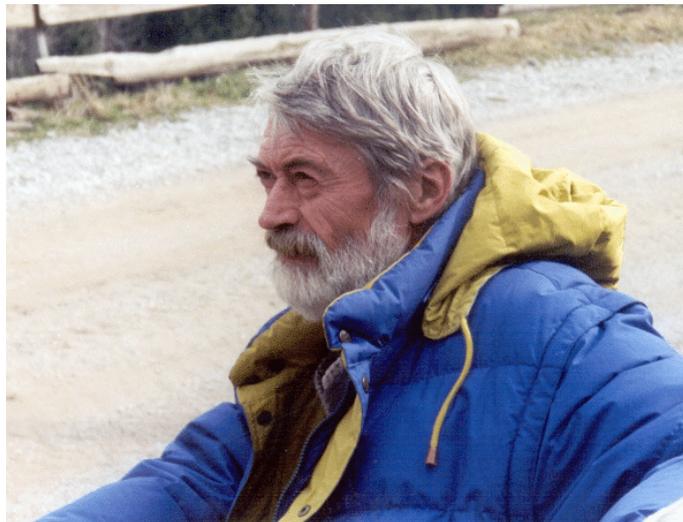
South Africa, see Fig. 15), although shifted towards higher fugacities. The above discussed similarities in metasomatic style recorded in the Ulten and Bardane peridotites, together with their relatively high fO_2 values compared to subcratonic mantle equilibrated at similar P, suggest a relevant similarity in the oxidizing metasomatic agents infiltrating the mantle wedge rocks at both settings. This observation points that comparable metasomatic processes driven by C-O-H fluid phases have affected the mantle wedge over a large range of subduction depths, from ~ 80 km (Ulten Zone) to ~200 km (Bardane).

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Figure 18. Lauro Morten (March 19, 1941 - November 18, 2006).



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